

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
22 February 2001 (22.02.2001)

PCT

(10) International Publication Number  
**WO 01/12554 A1**

- (51) International Patent Classification<sup>7</sup>: **C01F 7/34** TX 77586 (US). JONES, William; 56 Lantree Crescent, Cambridge CB2 2NJ (GB).
- (21) International Application Number: PCT/EP00/07792
- (22) International Filing Date: 11 August 2000 (11.08.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
09/372,557 11 August 1999 (11.08.1999) US
- (71) Applicant: AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).
- (72) Inventors: STAMIRE, Dennis; 6 Rockingham Drive, Newport Beach, CA 92660 (US). O'CONNER, Paul; Hogebrinkerweg 9, NL-3871 KM Hoevelaken (NL). PEARSON, Gregory; 1211 Goldendale Drive, Seabrook,
- (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).
- (81) Designated States (national): BR, CA, CN, IN, JP, KR.
- (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
- Published:**  
— With international search report.  
— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



**WO 01/12554 A1**

(54) Title: PROCESS FOR THE PREPARATION OF QUASI-CRYSTALLINE BOEHMITES

(57) Abstract: The present invention pertains to an improved process for the preparation of quasi-crystalline boehmite. In this improved process a quasi-crystalline boehmite precursor is aged at a pH below 7, preferably under hydrothermal conditions. It was found that when conducting the preparation processes for quasi-crystalline aluminas described in the prior art at a pH below 7 and under hydrothermal conditions instead of the high pH and thermal ageing used in the prior art, QCBs with higher crystallinity are obtained. In the process according to the invention additives may be added to the quasi-crystalline boehmite precursor. This results in a high quality QCB with additives in a homogeneously dispersed state. Suitable additives are compounds containing elements selected from the group of rare earth metals, alkaline earth metals, transition metals, actinides, silicon, gallium, boron, and phosphorus.

## PROCESS FOR THE PREPARATION OF QUASI-CRYSTALLINE BOEHMITES

## 5 BACKGROUND OF THE INVENTION

## Field of the Invention

The present invention pertains to a process for the preparation of quasi-crystalline boehmites.

10

## Description of the Prior Art

Alumina, alpha-monohydrates or boehmites and their dehydrated and or sintered forms are some of the most extensively used aluminum oxide-hydroxides materials. Some of the major commercial applications involve one or more forms of these materials and these are, for example, ceramics, abrasive materials, fire-retardants, adsorbents, catalysts, fillers in composites and so on. Also, a major portion of the commercial boehmite aluminas is used in catalytic applications such as refinery catalysts, catalyst for hydroprocessing hydrocarbon feeds, reforming catalysts, pollution control catalysts, cracking catalysts. The term "hydroprocessing" in this context encompasses all processes in which a hydrocarbon feed is reacted with hydrogen at elevated temperature and elevated pressure. These processes include hydrodesulphurisation, hydrodenitrogenation, hydrodemetallisation, hydrodearomatisation, hydro-isomerisation, hydrodewaxing, hydrocracking, and hydrocracking under mild pressure conditions, which is commonly referred to as mild hydrocracking. These types of aluminas are also used as catalysts for specific chemical processes such as ethylene-oxide production, and methanol synthesis. Relatively newer commercial uses of boehmite type of aluminas or modified forms thereof involve the transformation of environmentally unfriendly chemical components such as chlorofluorohydrocarbons (CFC's) and other undesirable pollutants. Boehmite

30

alumina types are further used as catalytic material for the treatment of exhaust gases of gas turbines for reducing nitrogen oxide.

5 The main reason for the successful extensive and diversified use of these materials in such variety of commercial uses, is their ability and flexibility to be "tailor" made to products with a very wide range of physical-chemical and mechanical properties.

10 Some of the main properties which determine the suitability of commercial applications involving gas-solid phase interactions such as catalysts and adsorbents are pore volume, pore size distribution, pore texture, specific density, surface areas, density and type of active centers, basicity and acidity, crushing strength, abrasion properties, thermal and hydrothermal aging (sintering) and long term stability.

15

To a large extent, the desired properties of the alumina product can be obtained by selecting and carefully controlling certain parameters which usually involve: raw materials, impurities, precipitation or conversion process conditions, aging conditions and subsequent thermal treatments (calcination/steaming) and  
20 mechanical treatments.

Nevertheless, in spite of all this large and diversified existing know-how, this technology still develops and presents unlimited scientific and technological challenges both to the manufacturers and end-users for further developments of  
25 such alumina based materials.

The term, boehmite, is used in the industry to describe alumina hydrates which exhibit XRD patterns close to that of the aluminum oxide-hydroxide [AlO(OH)], naturally occurring boehmite or diaspor. Further, the general term,

boehmite, usually is used to broadly describe a wide range of alumina hydrates which contain different amounts of water of hydration, have different surface areas, pore volumes, specific densities, and exhibit different thermal characteristics upon thermal treatments. Yet their XRD patterns, although they exhibit the characteristic boehmite  $[\text{AlO}(\text{OH})]$  peaks, usually vary in their widths and can also shift in their location. The sharpness of the XRD peaks and their location have been used to indicate degree of crystallinity, crystal size, and amount of imperfections.

10       Broadly, there are two categories of boehmite aluminas. Category I, in general, contains boehmites which have been synthesized and/or aged at temperatures close to  $100^{\circ}\text{C}$  and most of the time under ambient atmospheric pressures. In the present specification, this type of boehmite is referred to as quasi-crystalline boehmites. The second category of boehmite consists of so-called micro-crystalline boehmites.

      In the state of the art, category I boehmites, quasi-crystalline boehmites, are referred to, interchangeably as: pseudo-boehmites, gelatinous boehmites or quasi-crystalline boehmites (QCB). Usually these QCB aluminas have very high surface areas, large pores and pore volumes, lower specific densities than microcrystalline boehmites, disperse easily in water or acids, they have smaller crystal sizes than micro-crystalline boehmites, and contain a larger number of water molecules of hydration. The extent of hydration of the QCB can have a wide range of values, for example from about 1.4 up and about 2 moles of water per mole of  $\text{AlO}$ , intercalated usually orderly or otherwise between the octahedral layers.

The DTG (differential thermogravimetry) curves, which are the water release from the QCB materials as function of temperature, show that the major peak

appears at much lower temperatures as compared to that of the much more crystalline boehmites. The XRD Patterns of QCBs show quite broad peaks and their half-widths are indicative of the crystal sizes as well as degree of crystal perfection.

5

The broadening of the widths at half-maximum intensities varies substantially and typical for the QCB's could be from about  $2^\circ - 6^\circ$  to  $2\theta$ . Further, as the amount of water intercalated into the QCB crystals is increased, the main (020) XRD reflection moves to lower  $2\theta$  values corresponding to greater d-spacings. Some typical, commercially available QCB's are; Condea Pural®, Catapal® and Versal® products.

The category II of the boehmites consists of microcrystalline boehmites (MCB), which are distinguished from the QCBs due to their high degree of crystallinity, relatively large crystal sizes, very low surface areas, and high densities. Contrary to the QCB's the MCB's show XRD patterns with higher peak intensities and very narrow half-peak line widths. This is due to the relatively small number of water molecules intercalated, large crystal sizes, higher degree of crystallization of the bulk material and to lesser amount of crystal imperfections present. Typically, the number of molecules of water intercalated can vary in the range from about 1 up to about 1.4 per mole of  $\text{AlO}$ . The main XRD reflection peaks (020) at half-length of maximum intensities have widths from about  $1.5^\circ$  down to about  $0.1^\circ$  degrees  $2\theta$ . For the purpose of this specification we define quasi-crystalline boehmites to have 020 peak widths at half-length of the maximum intensity of  $1.5^\circ$  or greater than  $1.5^\circ$ . Boehmites having a (020) peak width at half-length of the maximum intensity smaller than  $1.5^\circ$  are considered micro-crystalline boehmites.

A typical MCB commercially available product is Condea's P-200 ® grade of alumina. Overall, the basic, characteristic differences between the QCB and MCB types of boehmites involve variations in the following: 3-dimensional lattice order, sizes of the crystallites, amount of water intercalated between the octahedral layers and degree of crystal imperfections.

Regarding the commercial preparation of these boehmite aluminas, QCB's are most commonly manufactured via processes involving: Neutralization of aluminum salts by alkalines, acidification of aluminate salts, hydrolysis of aluminum alkoxides, reaction of aluminum metal (amalgamated) with water and rehydration of amorphous rho-alumina obtained by calcining gibbsite. The MCB type of boehmite aluminas, in general are commercially produced with hydrothermal processes using temperatures usually above 150°C and autogeneous pressures. These processes usually involve hydrolysis of aluminum salts to form gelatinous aluminas, which are subsequently hydrothermally aged in an autoclave at elevated temperatures and pressures. This type of process is described in US 3,357,791. Several variations of this basic process exist involving different starting aluminum sources, additions of acids or salts during the aging, and a wide range of process conditions.

20

MCB's are also prepared using hydrothermal processing of gibbsite. Variations of these processes involve; addition of acids, alkaline and salts during the hydrothermal treatment, as well as the use of boehmite seeds to enhance the conversion of gibbsite to MCB. These types of processes are described in Alcoa's US 5,194,243, in US 4,117,105 and in US 4,797,139.

25

Nevertheless, whether pseudo-, quasi- or microcrystalline such boehmite materials are characterized by reflections in their powder X-ray. The ICDD contains entries for boehmite and confirms that reflections corresponding to the

(020) , (021) and (041) planes would be present. For copper radiation, such reflections would appear at 14, 28 and 38 degrees two theta.. The various forms of boehmite would be distinguished by the relative intensity and width of the reflections. Various authors have considered the exact position of the reflections in terms of the extent of crystallinity. Nevertheless, lines close to the above positions would be indicative of the presence of one or more types of boehmite phases.

10 In the prior art, we find QCB containing metal ions which have been prepared by the hydrolysis of alumina isopropoxide with the co-precipitation of lanthanides as described in the paper by J. Medena, J. Catalysis, vol. 37, 91- (1975), and J. Wachowski et al., Materials Chemistry, vol. 37, 29-38 (1994). This process is conducted at a pH above 7.0. The products are pseudo-boehmite type  
15 aluminas with the occlusion of one or more lanthanide metal ions. These materials have been primarily used in high temperature commercial applications where the presence of such lanthanide metal ions in the pseudo-boehmite structure retards the transformation of the gamma-alumina to the alpha-alumina phase. Therefore, a stabilization of the gamma phase is obtained, retaining a  
20 higher surface area before it converts to the refractory lower surface area alpha-alumina. Specifically Wachowski et al. used the lanthanide ions (La, Ce, Pr, Nd, Sm) in quantities from 1% to 10% by weight which were calcined at temperatures in the range of 500°C to 1200°C.

25 Also, EP-A1-0 597 738 describes the thermal stabilization of alumina by addition of lanthanum, optionally combined with neodymium. This material is prepared by aging rehydrateble alumina (i.e. flash calcined gibbsite) in a slurry at a pH between 8 and 12 with a lanthanum salt at a temperature between 70 and

110 °C, followed with thermal treatment at a temperature between 100 and 1000°C.

Further, EP-A-0 130 835 describes a catalyst comprising a catalytically active metal supported on a lanthanum or neodymium- $\beta$ -  $\text{Al}_2\text{O}_3$  carrier. Said carrier is obtained by precipitation of aluminum nitrate solution with ammonium hydroxide in the presence of a lanthanum, praseodymium or neodymium salt solution. As the precipitated amorphous material is directly washed with water and filtered, the alumina is not allowed under the usual conditions and certain pH, concentration and temperatures to age with time so that it crystallizes to a boehmite alumina structure.

#### SUMMARY OF THE INVENTION

The present invention is directed to an improved process for the preparation of quasi-crystalline boehmite. In this improved process a quasi-crystalline boehmite precursor is aged at a pH below 7, preferably under hydrothermal conditions.

Other objectives and embodiments of our invention encompass details about compositions, manufacturing steps, etc., all of which are hereinafter disclosed in the following discussion of each of the facets of the present invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is an X-ray diffractogram (XRD) for the spectrum of Catapal A® of Vista Chemicals.

FIGURE 2 is the XRD pattern of the QCB formed in the procedure of Example 2.

FIGURE 3 is the XRD pattern of the QCB formed in the procedure of Example 3.

FIGURE 4 is the XRD pattern of the QCB formed in the procedure of Comparative Example 4.



## DETAILED DESCRIPTION OF THE INVENTION

It was found that when conducting the preparation processes for quasi-  
5 crystalline aluminas at a pH below 7, preferably under hydrothermal conditions,  
instead of at a high pH in combination with the thermal aging as is described in  
the prior art, QCBs with higher crystallinity are obtained. Suitable quasi-crystalline  
boehmite precursors are aluminum alkoxide, soluble aluminum salts such as  
aluminum sulfate, aluminum nitrate, aluminum chloride and sodium aluminate,  
10 thermally treated aluminum trihydrate such as flash calcined aluminum trihydrate  
(CP ® alumina), amorphous gel alumina, QCBs with relatively low crystallinity,  
aluminum trihydrate such as gibbsite, BOC and bayerite and mixtures thereof,

In the process according to the invention additives may be added to the quasi-  
15 crystalline boehmite precursor. This results in a high quality QCB with additives in  
a homogeneously dispersed state. It was found that when using a pH below 7 the  
additives in the resulting QCB are even more homogeneously dispersed than  
when using the higher pH and thermal aging of the prior art processes. In fact, it  
was found that some additives can only be added in a homogeneously dispersed  
20 state at these low pHs such as lanthanum nitrate and nickel salts. At higher pHs,  
the additives precipitate readily as a separate phase. Additives present in QCB  
aid to adjust the QCBs physical, chemical and catalytic properties such as  
thermal stability, specific density, surface area, pore volume, pore size distribution,  
density and type of active centers, basicity and acidity, crushing strength,  
25 abrasion properties etcetera, and so determine the boehmite's suitability for use  
in catalytic or absorbent material. The fact that the additive is homogeneously  
dispersed within the QCB distinguishes the QCBs according to the invention from  
QCBs which have been impregnated with additives, and renders these new QCBs  
extremely suitable for catalytic purposes or as starting materials for the

preparation of catalysts for heterogeneous catalytic reactions. For the purpose of the invention, it is stated that a homogenous dispersion of the additive is present in the QCB if the X-ray diffraction pattern has no reflections of the additive, and thus the additive is not present as a separate phase. It is, of course, possible to  
5 incorporate different types of additives in the QCB according to the invention.

Suitable additives are compounds containing elements selected from the group of rare earth metals, alkaline earth metals, alkaline metals, transition metals, actinides, noble metals such as Pd and Pt, silicon, gallium, boron,  
10 titanium, and phosphorus. For instance, the presence of silicon increases the amount of acidic sites in the boehmite, transition metals introduce catalytic or absorbing activity such as  $\text{SO}_x$  captivation,  $\text{NO}_x$  captivation, hydrogenation, hydroconversion, and other catalytic systems for gas/solid interactions.

15 Suitable compounds containing the desired elements are nitrates, sulfates, chlorides, formates, acetates, carbonates, vanadates etcetera. The use of compounds with decomposable anions is preferred, because the resulting QCBs with additive may directly be dried, without any washing, as undesirable anions for catalytic purposes are not present.

20

The QCBs according to the invention may be prepared in several ways as long as the aging step is conducted at a pH below 7. The process is preferably conducted under hydrothermal conditions. In general a quasi-crystalline boehmite precursor and optionally additive are aged, preferably under hydrothermal conditions, to  
25 form a quasi-crystalline alumina. The aging may be conducted hydrothermally, which means in the presence of a protic liquid or gas such as water, ethanol, propanol or steam and under pressure, i.e. with increased pressure such as aging in water at a temperature above 100 °C under autogeneous pressure. Examples of suitable preparation processes are described below:

### Process 1

The QCB can be prepared by hydrolyzing and aging an aluminum alkoxide,  
5 preferably under hydrothermal conditions. Any additive can be incorporated during the hydrolysis step or added at the end before the aging step.

### Process 2

10 The QCB may be prepared by hydrolysis and precipitation as hydroxides of soluble aluminum salts and aged, preferably hydrothermally, to form a QCB. Examples of suitable aluminium salts are aluminum sulfate, aluminum nitrate, aluminum chloride, sodium aluminate, and mixtures thereof. The additive(s) may be added simultaneously during hydrolysis and coprecipitation or at the end in the  
15 aging step.

### Process 3

The QCB can also be prepared by aging a slurry containing a thermally  
20 treated form of aluminum trihydrate and optionally additive for a time sufficient to form QCB. Thermally treated forms of aluminum trihydrate are calcined aluminum trihydrate and flash calcined aluminum trihydrate (CP ® alumina). This preparation method has the advantage that no ions are introduced into the QCB besides ions of an optional additive compound. That means that with the  
25 appropriate choice of additive compounds washing steps can be reduced or avoided altogether. For instance, when additive compounds are used with decomposable anions (such as carbonates, nitrates and formates), the QCB containing additive may be dried directly, since undesirable cations for catalytic purposes will not be present. A further advantage of this preparation method is

that it is possible to first shape a slurry containing a thermally treated form of aluminum trihydrate and optionally additive, reslurry the shaped bodies, and subsequently age the shaped bodies to form QCB. Shaping is defined in this specification as any method of obtaining particles with the appropriate size and strength for the specific purpose. Suitable shaping methods are spray-drying, extrusion (optionally with intermediate spray-drying, filterpressing, or kneading), pelletizing, beading or any other conventional shaping method used in the catalyst field.

#### 10 Process 4

The QCB can also be prepared by aging a slurry containing amorphous gel alumina and optionally additive(s) for a time sufficient to form QCB. Like process 4 mentioned above, this preparation method has also the advantage that no ions are introduced into the QCB beside optionally any ions of the additive compound. That means that with the appropriate choice of additive compounds washing steps can be reduced or avoided altogether. Also it is possible to first shape a slurry containing amorphous alumina gel and optional additive, reslurry the shaped bodies, and subsequently age the shaped bodies to form QCB. In this case care must be taken to choose a shaping step in which the amorphous gel alumina/additive mixture are not heated to temperature exceeding the aging temperature.

#### Process 5

25

QCBs according to the invention may also be prepared by aging, preferably by hydrothermal treatment, a relatively amorphous QCB, optionally in the presence of compounds of a desired additive. The crystallinity increases to some extent, but the resulting product is still a QCB according to the definition of the present

description. This process also allows shaping of the QCB-additive mixture before the thermal treatment. Further, no additional ions besides the optional ions of the additive compound are introduced in the QCB.

## 5 Process 6

QCBs may also be prepared by aging, preferably by hydrothermal treatment alumina trihydrates such as gibbsite, BOC and bayerite, with the help of suitable boehmite seeds in the presence of compounds of the desired additives. Suitable  
10 seeds are the known seeds to make microcrystalline boehmite such as commercially available boehmite (Catapal ®, Condea ®Versal, P-200 ® etcetera), amorphous seeds, milled boehmite seeds, boehmite prepared from sodium aluminate solutions, etcetera. Also quasi-crystalline boehmites prepared by one of the processes described here can suitably be used as a seed. It was  
15 found that aging at a pH below 7 favors the production of QCBs over MCBs. Like processes 3, 4, and 5 no additional ions besides the optional ions of the additive are introduced into the QCB, and this process allows shaping prior to the aging step.

20 Although, processes 5 and 6 described-above are known for the preparation of microcrystalline boehmites, we found that aging at a pH below 7 favors the production of QCBs over MCBs. Further, the process can be adapted to form QCBs by adjusting the seed and the conditions used.

25 The first publications on the use of seeds in the hydrothermal conversion of aluminum trihydrate date back in the late 1940's/early 1950's. For example, G. Yamaguchi and K. Sakamoto (1959), clearly demonstrate the concept that boehmite seeds substantially improved the kinetics of the hydrothermal

conversion of gibbsite to boehmite, by lowering the temperature, shorten the reaction time, and increase the gibbsite conversion.

Also the beneficial principle of seeding with boehmite in the hydrothermal

5 transformation of gibbsite in an autoclave operating at elevated temperatures and autogeneous pressures was also demonstrated clearly by G. Yamaguchi and H. Yamanida (1963).

There are several other publications in the open literature, in which equally  
10 well the benefits of seeding with boehmite and/or alkaline solutions are demonstrated. Further, the use of boehmite seed is also claimed to produce finer particle size boehmite product which is easier to disperse in water. The use of boehmite seeds in the hydrothermal conversion of gibbsite has been described in US 4,797,139, filed on December 16, 1987, and in US 5,194,243, filed on  
15 September 30, 1985.

In all the above- described processes an intermediate calcination step, prior to the aging step may be applied.

20 All the processes described above may be conducted batch-wise or in a continuous mode, optionally in a continuous multy step operation. The processes may be conducted partly continuous, partly batchwise.

As mentioned-above, more than one type of QCB precursor may be used,  
25 although care must be taken that the reaction conditions employed enable the conversion of the precursor to QCB. Said mixture of QCB precursors may be prepared before introduction of the additive or the various types of precursors may be added in any of the further stages of the reaction.

In the processes for the preparation of the QCBs according to the invention more than one aging step may be applied, wherein for instance the aging temperature and/or condition (thermally or hydrothermally, pH, time) is varied.

5           The reaction products of the processes for the preparation of the QCBs according to the invention may also be recycled to the reactor.

          If more than one type of additive is incorporated into the QCB, the various additives may be added simultaneously or sequentially in any of the reaction  
10   steps.

          It may be advantageous to add acids or bases to adjust the pH during the hydrolysis and/or precipitation.

15           As mentioned-above some of the processes for the preparation of the quasi-crystalline boehmites according to the invention allow shaping into shaped bodies during preparation. It is also possible to shape the final QCB, optionally with the help of binders and/or fillers. The invention is also directed to shaped bodies obtained with the process according to the invention.

20           As mentioned above, the QCBs according to the invention are extremely suitable as components or starting material for catalyst compositions or catalyst additives. To this end the QCB is combined with, optionally, binders, fillers ( e.g. clay such as kaolin, titanium oxide, zirconia, silica, silica-alumina, bentonite etcetera), catalytically active material such as molecular sieves (e.g.ZSM-5,  
25   zeolite Y, USY zeolite), and any other catalyst components such as for instance pore regulating additives, which are commonly used in catalyst compositions. For some applications it may be advantageous to neutralise the QCB before use as catalyst component, for instance to improve or create pore volume. Further, it is preferred to remove any sodium to a content below 0.1 wt% Na<sub>2</sub>O. The present

invention therefore is also directed to catalyst compositions and catalyst additives comprising the QCB according to the invention.

5 In a further embodiment of the invention, the QCB may be mixed with other metal oxides or hydroxides, binders, extenders, activators, pore regulating additives, etcetera in the course of further processing to produce absorbents, ceramics, refractories, substrates, and other carriers.

10 For catalytic purposes, boehmites are generally used at temperatures between 200 and 1000°C. At these high temperatures the boehmites are usually converted into transition-aluminas. Therefore, the present invention is also directed to transition alumina which is obtainable by thermal treatment of the quasi-crystalline boehmite prepared with the process according to the invention

15 With the above-mentioned transition aluminas catalyst compositions or catalyst additives can be made, optionally with the help of binder materials, fillers, etcetera.

20 The present invention will be illustrated by means of the following non-limiting examples.

## EXAMPLES

### 25 Comparative example 1

An XRD pattern of a sample of commercially available quasi-crystalline boehmite, Catapal A ® is given in Figure 1.



### Comparative example 2

A quasi-crystalline boehmite was prepared from hydrolysis of aluminum isopropoxide and aged at 65 °C for 5 days. The XRD pattern is given in Figure 2.

5

### Example 3

The product of Comparative example 4 reslurried in water and aged at a pH of 4 at a temperature of 198 °C for 1 hour. The XRD pattern is shown in Figure 3.

10

### Comparative example 4

A quasi-crystalline boehmite was produced using the process of Wachowski containing 5 wt% lanthanum ions (calculated at the oxide). The XRD pattern is given in Figure 4.

15

### Example 5

The product of Comparative example 4 was re-slurried in water, the pH was adjusted to 4 and the slurry was hydrothermally treated at 198 °C for 1 hour. Comparison of the XRD of the product of example 4 and the XRD of the product of example 5 shows that when using the hydrothermal conditions and low pH according to the process of the invention, an improved crystallinity is obtained.

20

### Example 6

5 wt% lanthanum nitrate (calculated as the oxide) in solution was added to a slurry containing fine particle Gibbsite and 20% Catapal A alumina ® as a seed. The pH was adjusted between 4 and 6 and homogenized. In an autoclave the resulting slurry was heated to 180 °C for 2 hours under autogeneous pressure.

30

Example 7

Example 1 was repeated using finely ground BOC. 10 wt% of Catapal A, strongly  
5   peptized with nitric acid, was used as a seed. The pH was adjusted to 6, and 10  
wt% lanthanum nitrate (calculated as oxide) in solution was added. The resulting  
slurry was homogenized in a blender and transferred to an autoclave where it was  
heated under autogeneous pressure to 175 °C for 2 hours.

10   Example 8

Example 6 was repeated using sodium aluminate (10 wt% calculated as alumina)  
as a seed. The pH was adjusted between 6 and 7 with nitric acid, and 5 wt%  
lanthanum nitrate (calculated as oxide) in solution was added. The resulting slurry  
15   was homogenized in a blender and transferred to an autoclave where it was  
heated under autogeneous pressure to 165 °C for 2 hours.

## Claims

1. A process for the preparation of quasi-crystalline boehmite wherein a quasi-crystalline boehmite precursor is aged at a pH below 7.  
5
2. The process of claim 1 wherein the aging is conducted under hydrothermal conditions.
- 10 3. A process according to any one of the claims 1-2 wherein the quasi-crystalline boehmite precursor is aged in the presence of an additive.
4. A process according to any one of the claims 1-3 wherein the additive is a compound containing an element selected from the group of rare earth metals,  
15 alkaline earth metals, transition metals, actinides, silicon, boron, and phosphorus.
5. A process according to any one of the claims 1-3 wherein more than one type of quasi-crystalline boehmite precursor is used.  
20
6. A process according to any one of the claims 1-3 wherein aluminum alkoxide is hydrolyzed and aged to form quasi-crystalline boehmite containing additive.
7. A process according to any one of the claims 1-3 wherein a soluble aluminum  
25 salt is hydrolyzed and precipitated as a hydroxide to obtain said quasi-crystalline boehmite precursor, followed by aging to form a quasi-crystalline boehmite.

8. A process according to any one of the claims 1-3 wherein thermally treated aluminum trihydrate is rehydrated in water to obtain a slurry which comprises said quasi-crystalline boehmite precursor, followed by aging for a time sufficient to form said quasi-crystalline boehmite.

5

9. A process according to any one of the claims 1-3 wherein amorphous gel alumina is slurried in water in the presence of an additive to obtain said quasi-crystalline boehmite precursor which is aged for a time sufficient to form said quasi-crystalline boehmite.

10

10. A process according to any one of the claims 1-3 wherein said precursor comprises aluminum trihydrate and a boehmite seed which are aged to form said quasi-crystalline boehmite.

11. A process according to any one of the claims 1-10 wherein the quasi-crystalline boehmite precursor is shaped into a shaped body prior to aging.

12. A process according to any one of the claims 1-11 which is conducted in a continuous mode.

20

13. A process according to any one of the claims 1-12 wherein said preparation is carried out in a reactor and the reaction products are recycled to said reactor.

14. A process according to any one of the claims 1-13 wherein more than one aging step is used.

25

15. A process according to any one of the claims 1-10 and 12-14 wherein the quasi-crystalline boehmite formed in the aging step is shaped into a shaped body.

16.A process for the preparation of transition alumina by thermal treatment of a quasi-crystalline boehmite prepared according to any one of the processes of claims 1-15.

Figure 1. XRD of Catapal

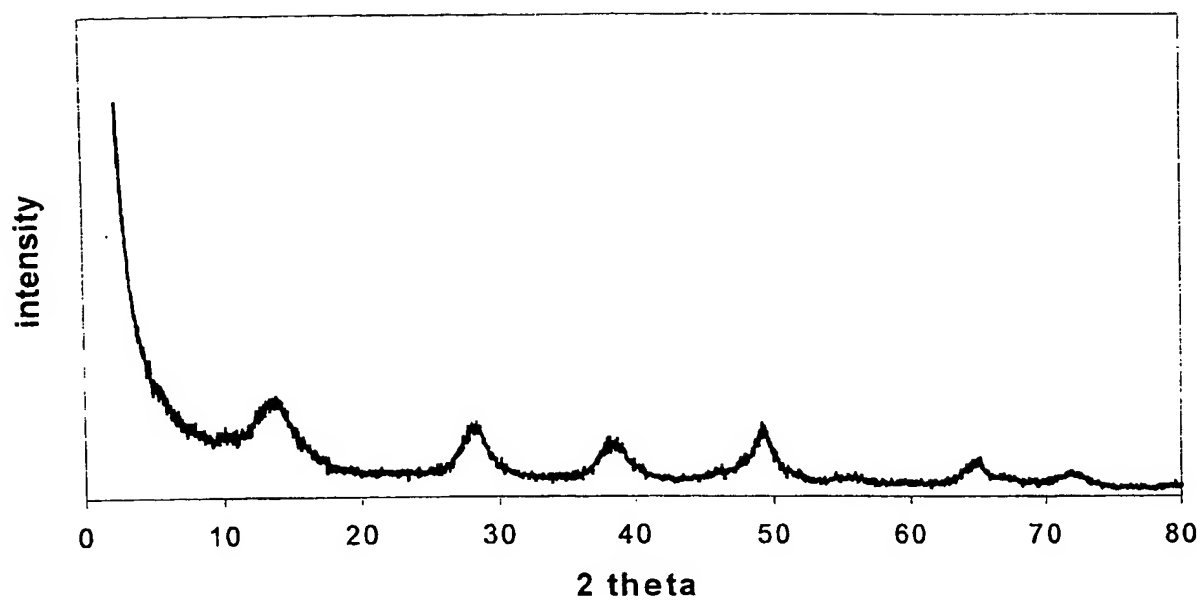


Figure 2 QCB prepared from Al isopropoxide and thermal aging

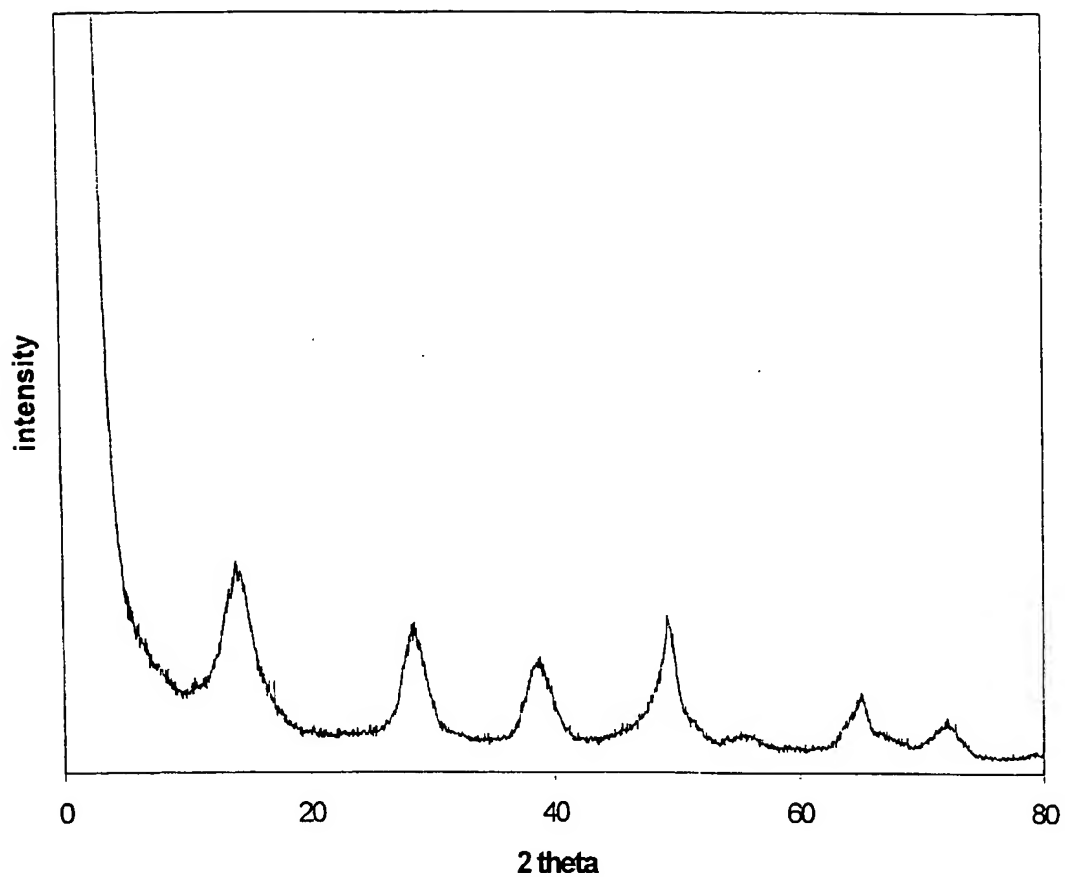


Figure 3 QCB prepared by hydrothermal treatment at pH=4

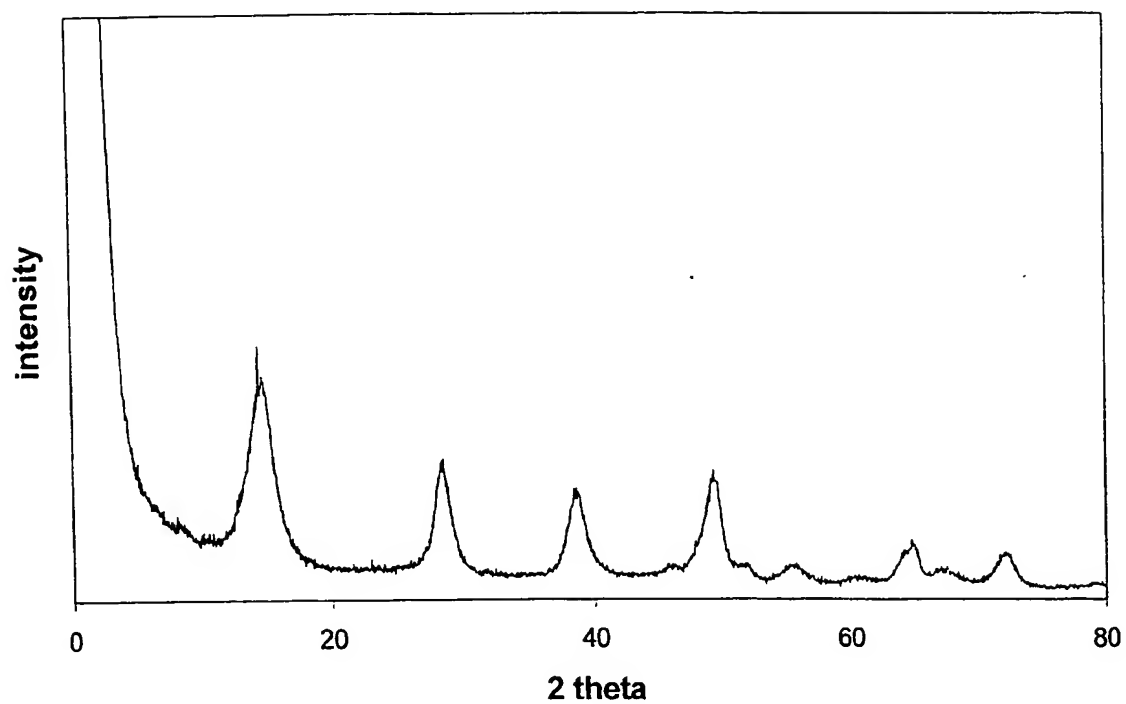
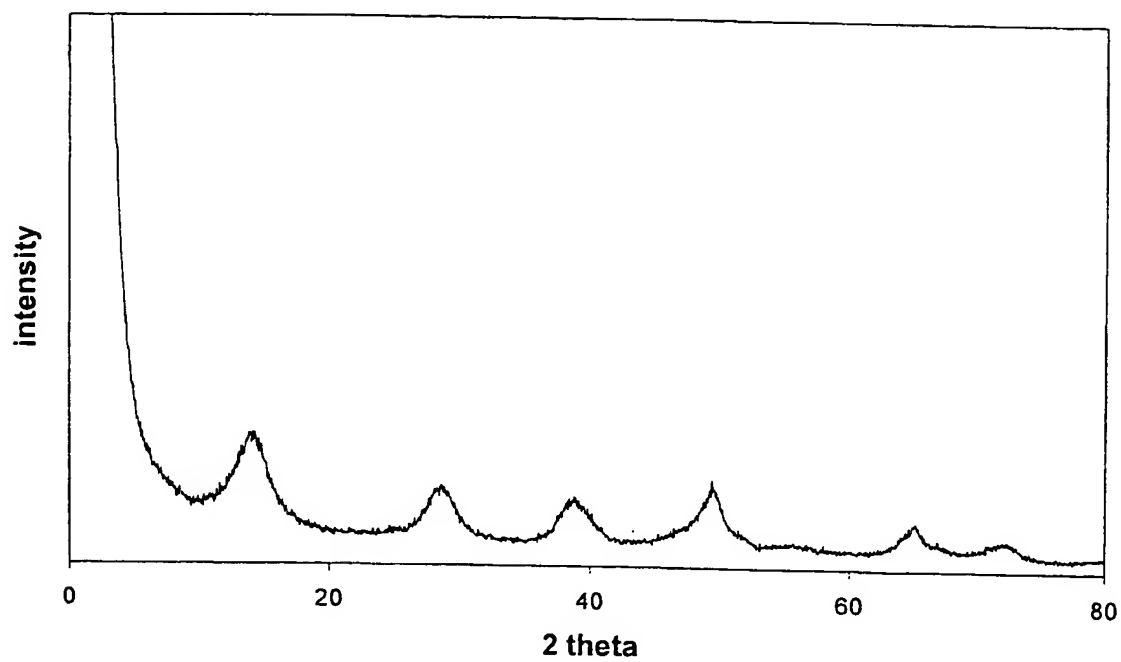




Figure 4 QCB prepared with Wachowski process



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/07792

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01F7/34

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 113 796 A (DEGUSSA) 25 July 1984 (1984-07-25) page 2, line 20 -page 3, line 21 ---	1
A	US 3 739 062 A (BARSOTTI L) 12 June 1973 (1973-06-12) example 1 ---	1
A	US 4 344 928 A (DUPIN THIERRY ET AL) 17 August 1982 (1982-08-17) claim 1 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 09, 31 July 1998 (1998-07-31) & JP 10 109030 A (JAPAN ENERGY CORP), 28 April 1998 (1998-04-28) abstract --- -/--	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

18 December 2000

Date of mailing of the international search report

28/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Clement, J-P

# INTERNATIONAL SEARCH REPORT

Inter. . . onal Application No

PCT/EP 00/07792

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 332 782 A (SCHERZER JULIUS ET AL)</p> <p>1 June 1982 (1982-06-01)</p> <p>column 2, line 43 - line 64</p> <p style="text-align: center;">-----</p>	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/07792

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0113796	A	25-07-1984	DE 3243193 A CA 1246833 A DE 3369114 D	30-05-1984 20-12-1988 19-02-1987
US 3739062	A	12-06-1973	NONE	
US 4344928	A	17-08-1982	FR 2449650 A BR 8001095 A CA 1153187 A DE 3060286 D EP 0015196 A ES 488888 A JP 1240927 C JP 55116622 A JP 59013446 B MX 6585 E	19-09-1980 29-10-1980 06-09-1983 27-05-1982 03-09-1980 16-09-1980 26-11-1984 08-09-1980 29-03-1984 25-07-1985
JP 10109030	A	28-04-1998	NONE	
US 4332782	A	01-06-1982	NONE	